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A Four-Parameter Corresponding-States Method for Prediction of Newtonian, Pure-Component Viscosity

K. J. Okeson[1,2] **and R. L. Rowley**[1]

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The extended Lee–Kesler (ELK) method, introduced for calculating thermodynamic properties of polar as well as nonpolar fluids and their mixtures, has been adapted to the calculation of Newtonian, pure-fluid viscosity. The method is a four-parameter, corresponding-states technique requiring as input the critical temperature, critical pressure, a size/shape parameter α, and a polar interaction parameter β. Because α and β have been previously tabulated for many fluids (for calculation of thermodynamic properties) and may also be obtained directly from the radius of gyration and a single liquid density, respectively, the method contains no adjustable parameters and is predictive in nature. ELK viscosity predictions were compared to experimental data for nonpolar and polar fluids. For 36 different nonpolar fluids and a total of 5748 different points, the comparison yielded an absolute average deviation (AAD) of 7.88% with a bias of −4.45%. Similarly, the AAD was 10.62% with a bias of −5.34% for a comparison of 15 different polar fluids involving 1500 different points. With this method, viscosities can be calculated within the range $0.55 \leqslant T_r \leqslant 2.00$ and $0 < P_r \leqslant 10$.

KEY WORDS: corresponding states; Lee–Kesler method; polar fluids; viscosity.

1. INTRODUCTION

Inconsistency between calculated properties is often a problem in industrial thermophysical property simulators because different prediction methods are used for different properties. For example, the enthalpy predictor may

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[1] Department of Chemical Engineering, 350 CB, Brigham Young University, Provo, Utah 84602, U.S.A.

[2] Present address: Dow Corning Corporation, P.O. Box 310, Carrollton, Kentucky 41008, U.S.A.

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produce a liquid property in a region where the vapor pressure equation indicates a gas phase should be present. A consistent method that can be used to calculate all the desired thermophysical properties from one set of fundamental constants would be convenient. The Lee–Kesler (LK) corresponding-states technique for prediction of thermodynamic properties of nonpolar fluids has found widespread use in property simulators since its introduction by Lee and Kesler [1] and is a probable candidate for such a generalized method. Wilding and Rowley [2] extended the LK method to pure-component polar fluids, and Wilding et al. [3] used this so-called extended Lee–Kesler (ELK) method to calculate vapor pressures. Recently, mixing rules have been developed for ELK which permit prediction of vapor–liquid equilibria in highly nonideal binary [4] and ternary [5] mixtures.

Corresponding-states techniques have been among the most fruitful methods for predicting transport properties. Of these, TRAPP [6] is perhaps the most widely used for nonpolar fluids. A variation of TRAPP for viscosity predictions of polar fluids was recently introduced by Hwang and Whiting [7]. Unfortunately, a viscosity acentric factor, different in value from the acentric factor used to calculate thermodynamic properties, is required in the latter method. A purely predictive method for polar-fluid transport properties which uses the same fundamental constants required for thermodynamic property calculation is certainly desirable.

In this study, ELK was chosen as the basis for a viscosity computational method because of its separation, at least in theory, of purely size/shape effects from polar effects. It was hoped that this separation would enable calculation of fluid viscosities over a wide range of conditions using the same constants and procedures as are currently used to predict equilibrium properties within the framework of the Lee–Kesler method.

2. ELK

2.1. Previous Development for Equilibrium Properties

In LK calculations, deviations from simple two-parameter corresponding states are attributed to acentric molecular interactions. In ELK, the molecular size/shape effects of nonpolar fluids are distinguished from effects due to oriented interactions, including dipole and weak associations. Thus, ELK can be viewed as a perturbation about a spherically symmetric reference fluid in terms of size/shape, α, and polar, β, parameters. At a given reduced temperature and pressure, any dimensionless configurational property of the fluid, J, may be expressed as a Taylor's series expansion about the simple fluid, which when truncated to linear terms is

$$J = J_0 + \left(\frac{\partial J}{\partial \alpha}\right)_{T_r, P_r, \beta} (\alpha - \alpha_0) + \left(\frac{\partial J}{\partial \beta}\right)_{T_r, P_r, \alpha} (\beta - \beta_0) + \mathcal{O}(\alpha^2, \beta^2, \alpha\beta) \quad (1)$$

The derivatives in Eq. (1) are evaluated using linear difference expressions in terms of known properties of reference fluids. As in the LK method, methane is used as the simple, spherical reference fluid (denoted as reference fluid 0 in the above expansion) and *n*-octane is used as reference fluid 1 to quantify deviations from the spherical case. In ELK, water is used as reference fluid 2 to account for polar effects upon properties. Reasonably accurate equations of state are used to calculate the properties of each real reference fluid at the desired reduced conditions, and the contributions are summed to provide a value for the unknown fluid at these conditions. Thus,

$$J = J_0 + \alpha\left(\frac{J_1 - J_0}{\alpha_1}\right) + \frac{\beta}{\beta_2}\left\{J_2 - \left[J_0 + \alpha_2\left(\frac{J_1 - J_0}{\alpha_1}\right)\right]\right\} \quad (2)$$

or, more simply,

$$J = J^{(0)} + \alpha J^{(1)} + \beta J^{(2)} \quad (3)$$

where superscript (i) indicates the deviation of J for reference fluid i (scaled by the difference in either α or β) from J for the simple reference fluid, J_0, at the same reduced conditions. The simple reference fluid is assumed to obey two-parameter corresponding states. The deviation terms are computed from equations for the reference fluids in accordance with Eq. (2).

Values for α have been correlated in terms of the radius of gyration [2] to avoid inclusion of polar contributions and retain the integrity of the expansion shown in Eq. (1). Values for β were calculated from a single liquid density using $J = Z$ in the above equations. Here Z is the compressibility factor. Values for α and β have been compiled [3] for many components.

2.2. Extension to Viscosity

Use of Eq. (3) to calculate shear viscosity, η, requires (1) a choice for the dimensionless property J, (2) equations for the reference fluid viscosities valid over a wide range of T_r and P_r, and (3) values of α and β. The reduced viscosity is commonly defined as

$$\eta_r = \eta\xi \quad (4)$$

where

$$\xi = \left[\frac{RT_c N_0^2}{P_c^4 M^3} \right]^{1/6} \qquad (5)$$

A polynomial form for the real reference fluids' viscosity, shown in Table I, was obtained from Haar et al. [8]. The constants for water were obtained from the same source [8], while those for methane were regressed from experimental data obtained from the literature [9–14]. Due to the paucity of experimental data for *n*-octane, low-density Chapman–Enskog values and dense-gas values above $T_r = 1$, estimated from the method of Jossi et al. [15], were used to supplement experimental viscosities [10, 16–19]. The resulting equation is valid in the range $0 < P_r \leqslant 10$ and $0.55 \leqslant T_r \leqslant 2$, the intersection of the domains over which values were used to regress constants for the equations of the three reference fluids. The reference fluid equations represent available data quite well over the indicated domain except for the near-critical region. No critical enhancement was included. Graphical comparisons of experimental data and the equations in Table I over the applicability domain are available [20] and are not included here.

Although adjusting α and β to values unique for viscosity calculations would provide more flexibility and probably better agreement with experimental data, consistency of these parameters with equilibrium property calculations was considered essential. Unfortunately, water associates obscuring the appropriate value of α for use in viscosity calculations. In order to maintain the same set of α and β values for viscosity that are used in equilibrium property calculations, a value of -0.38 was required for α_2. The choice of water for the polar reference fluid was necessitated by the paucity of viscosity data for all other polar fluids over the desired T_r and P_r range.

Computation of viscosity for a test fluid from Eq. (3) is conveniently performed with a computer program containing the reference fluid equations of state. Required input includes T_c, P_c, radius of gyration (or, equivalently, α), and a liquid density (or, equivalently, β). The reference fluid equations are in terms of T_r and ρ_r rather than T_r and P_r. Thus, the reference-fluid equations of state are first solved for densities at the input T and P conditions. The results presented in this paper were obtained from the computer implementation of Eq. (3). However, one can also make quick hand calculations with ELK using Tables II–VII, which contain reduced simple-fluid, size/shape deviation, and polar deviation terms as a function temperature and pressure. The saturation line separating liquid- and vapor-phase values was drawn at the same locations as in previous LK tables for consistency. However, when using Tables II–VII, one must exer-

Table I. Real-Fluid Viscosity Reference Equations

I. Equation

$$\eta(\rho, T) = \eta^0(T) \exp\left[\left(\frac{\rho}{\rho^*}\right) \sum_{i=0}^{l} \sum_{j=0}^{m} b_{ij} \left(\frac{T^*}{T} - 1\right)^i \left(\frac{\rho}{\rho^*} - 1\right)^j\right]$$

$$\eta^0(T) = \left(\frac{T}{T^*}\right)^{1/2} \left[\sum_{k=0}^{n} a_k \left(\frac{T^*}{T}\right)^k\right]^{-1}$$

II. Critical Constants

	Methane	*n*-Octane	Water
T^*	190.7 K	568.8 K	6647.27 K
ρ^*	0.16205 g · cm^{-3}	0.23217 g · cm^{-3}	0.317763 g · cm^{-3}

III. Coefficients a_k

k	Methane	*n*-Octane	Water
0	0.00643022	0.00642742	0.0181583
1	0.00960573	0.00309416	0.0177624
2	−0.00353855	0.00045200	0.0105287
3	0.00081493	−0.00013078	−0.0036744

IV. Coefficients b_{ij}

$i\backslash j$	0	1	2	3	4
			(A) Methane		
0	0.638016	0.029595	0.146250	0.511526	−0.3972737
1	0.799681	−3.989641	0.301287	5.569193	−2.5482398
2	14.746602	−21.865741	−14.117418	23.074331	−5.1006388
3	55.551431	−35.267714	−46.449877	37.476870	−7.3272599
4	55.721564	−12.576820	−37.083285	22.909872	−3.7505328
			(B) *n*-Octane		
0	0.966135	−0.131849	0.039584	0.256352	−0.1221866
1	1.579156	−1.461535	−1.396700	2.060335	−0.4747973
2	10.175758	−7.421997	−10.647996	10.366272	−2.4223190
3	28.516915	−13.452535	−21.467961	17.041952	−3.1071504
4	25.579042	−8.380997	−13.578572	7.785231	−1.0881270
			(C) Water		
0	0.501938	0.235622	−0.274637	0.145831	−0.0270448
1	0.162888	0.789393	−0.743539	0.263129	−0.0253093
2	−0.130356	0.673665	−0.959456	0.347247	−0.0267758
3	0.907919	1.207552	−0.687343	0.213486	−0.0822904
4	−0.551119	0.0670665	−0.497089	0.100754	0.0602253
5	0.146543	−0.084337	0.195286	−0.032932	−0.0202595

Table II. Simple Fluid Values for $(\eta\xi)^{(0)} \times 10^{-3}$

	P_r														
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80	1.0	1.2	1.5	2.0	3.0	5.0	7.0	10.0
0.55	349	11389	11402	11429	11491	11560	11636	11721	11812	11962	12244	12922	14670	16850	20694
0.60	381	9171	9185	9214	9276	9343	9415	9492	9574	9705	9944	10487	11782	13261	15591
0.65	412	406	7419	7452	7522	7595	7670	7749	7830	7956	8177	8649	9668	10701	12094
0.70	443	435	444	6095	6175	6257	6340	6424	6509	6639	6858	7301	8164	8935	9789
0.75	473	465	465	5031	5124	5217	5310	5403	5496	5634	5862	6301	7086	7706	8260
0.80	502	496	493	510	4259	4367	4474	4578	4681	4833	5076	5528	6282	6820	7213
0.85	531	526	523	529	3487	3618	3743	3865	3982	4152	4418	4896	5648	6146	6460
0.90	559	556	554	555	592	2887	3048	3197	3338	3535	3835	4349	5118	5600	5885
0.93	576	574	572	573	597	676	2610	2792	2956	3178	3505	4048	4831	5312	5595
0.95	587	585	584	585	604	662	2280	2504	2694	2940	3291	3856	4650	5131	5418
0.97	598	596	596	597	613	658	774	2182	2417	2699	3080	3670	4476	4958	5251
0.98	603	602	601	603	618	658	753	1994	2268	2576	2975	3579	4392	4874	5171
0.99	609	608	607	609	623	659	740	1760	2109	2450	2871	3489	4308	4792	5092
1.00	614	613	613	615	629	662	731	1152	1934	2321	2766	3401	4226	4711	5016
1.01	620	619	619	621	634	665	726	891	1732	2187	2662	3314	4146	4631	4941
1.02	625	625	625	627	640	668	723	849	1487	2047	2558	3228	4067	4553	4867
1.05	641	641	642	644	657	681	723	801	987	1601	2245	2980	3838	4326	4655
1.10	668	668	670	673	685	706	739	790	874	1130	1757	2596	3482	3971	4325
1.15	694	695	697	701	714	734	762	803	862	1007	1431	2261	3162	3645	4018
1.20	720	722	724	729	742	761	787	822	870	974	1268	1990	2878	3348	3735
1.30	771	773	776	781	795	813	836	865	901	972	1145	1640	2419	2849	3241
1.40	822	824	826	832	846	863	883	907	936	990	1110	1451	2089	2469	2845
1.50	871	873	876	882	894	910	927	948	971	1013	1103	1347	1856	2192	2547
1.60	920	922	925	930	942	955	970	988	1007	1041	1109	1290	1695	1996	2335
1.70	968	970	972	977	988	1000	1013	1028	1044	1071	1125	1263	1591	1864	2195
1.80	1015	1017	1019	1024	1034	1045	1056	1069	1082	1105	1148	1257	1529	1782	2114
1.90	1062	1063	1066	1070	1080	1089	1100	1110	1122	1141	1177	1267	1499	1740	2083
2.00	1107	1109	1111	1116	1125	1134	1143	1153	1163	1180	1211	1289	1496	1730	2091

Table III. Size/Shape Deviation Values for $(\eta\xi)^{(1)} \times 10^{-3}$

	P_r														
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80	1.0	1.2	1.5	2.0	3.0	5.0	7.0	10.0
0.55	−55	33845	33884	33959	34097	34219	34328	34422	34503	34600	34701	34689	33902	32225	28405
0.60	−70	23979	23996	24026	24081	24126	24162	24190	24211	24229	24225	24114	23576	22793	21600
0.65	−80	−53	18014	18018	18022	18022	18018	18010	17998	17976	17927	17800	17532	17408	17868
0.70	−87	−60	−54	13780	13750	13719	13687	13654	13621	13572	13492	13356	13258	13523	14859
0.75	−93	−67	−49	10500	10443	10387	10333	10280	10230	10158	10052	9897	9884	10352	12095
0.80	−98	−74	−52	−33	7813	7733	7658	7586	7519	7426	7292	7110	7119	7674	9555
0.85	−103	−82	−59	−26	5752	5644	5544	5452	5367	5251	5088	4872	4869	5437	7296
0.90	−108	−89	−68	−31	24	4059	3922	3802	3695	3555	3364	3115	3084	3623	5367
0.93	−112	−94	−74	−37	24	105	3160	3012	2889	2732	2527	2264	2217	2728	4375
0.95	−114	−98	−78	−42	21	91	2739	2556	2417	2251	2039	1772	1718	2208	3783
0.97	−116	−101	−82	−47	16	82	251	2141	1985	1813	1601	1335	1276	1745	3245
0.98	−118	−102	−84	−50	13	78	192	1940	1774	1606	1397	1135	1076	1534	2996
0.99	−119	−104	−86	−53	10	73	165	1721	1557	1402	1203	948	889	1337	2759
1.00	−120	−106	−89	−55	7	69	149	862	1312	1198	1017	772	715	1152	2535
1.01	−121	−108	−91	−58	3	64	136	277	967	987	838	606	553	980	2323
1.02	−123	−109	−93	−61	−1	59	126	223	365	760	665	451	402	819	2123
1.05	−127	−115	−99	−70	−13	43	100	159	159	49	177	43	15	405	1591
1.10	−134	−124	−111	−85	−34	15	62	104	125	11	−310	−452	−441	−90	910
1.15	−142	−133	−122	−100	−56	−14	26	59	79	42	−264	−691	−706	−387	444
1.20	−150	−143	−133	−114	−77	−41	−8	20	38	25	−172	−694	−822	−537	146
1.30	−169	−163	−157	−143	−116	−89	−65	−44	−29	−26	−100	−474	−762	−557	−105
1.40	−189	−185	−180	−171	−151	−130	−111	−93	−79	−67	−87	−281	−539	−400	−107
1.50	−211	−208	−205	−198	−182	−166	−149	−132	−117	−99	−88	−158	−313	−211	−22
1.60	−234	−232	−230	−225	−212	−197	−181	−164	−148	−124	−94	−86	−135	−52	65
1.70	−258	−257	−255	−251	−240	−226	−210	−193	−174	−146	−103	−46	−13	60	119
1.80	−284	−283	−281	−277	−267	−253	−237	−218	−199	−167	−115	−28	63	126	128
1.90	−310	−309	−308	−304	−293	−279	−262	−243	−222	−188	−130	−24	101	152	93
2.00	−337	−336	−335	−331	−319	−305	−287	−267	−245	−209	−148	−32	111	146	18

Table IV. Polar Deviation Values for $(\eta\xi)^{(2)} \times 10^{-3}$

	P_r														
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80	1.0	1.2	1.5	2.0	3.0	5.0	7.0	10.0
0.55	17	12972	12984	13003	13032	13048	13050	13040	13018	12962	12815	12328	10683	8280	3629
0.60	20	8083	8085	8088	8085	8074	8054	8026	7991	7924	7780	7385	6266	4870	2660
0.65	27	29	5650	5637	5607	5572	5531	5487	5438	5358	5209	4866	4096	3359	2653
0.70	37	46	26	4179	4123	4066	4006	3945	3882	3786	3622	3295	2716	2359	2469
0.75	49	60	57	3186	3108	3029	2951	2874	2796	2682	2498	2160	1673	1520	2043
0.80	62	73	77	56	2384	2285	2188	2093	2000	1866	1657	1296	840	786	1492
0.85	77	86	93	92	1896	1771	1652	1537	1428	1272	1035	642	184	168	927
0.90	92	99	107	114	94	1466	1312	1171	1040	859	592	166	−306	−318	416
0.93	101	108	115	123	120	90	1198	1031	882	683	397	−47	−528	−546	151
0.95	107	113	120	129	132	114	1166	967	802	589	291	−163	−649	−671	−6
0.97	113	119	125	135	142	133	147	923	736	508	200	−261	−749	−778	−147
0.98	116	122	128	137	146	141	135	906	704	471	159	−304	−791	−823	−211
0.99	119	125	130	140	149	147	139	885	668	433	120	−343	−830	−865	−271
1.00	123	128	133	142	153	153	145	485	615	393	83	−379	−864	−902	−327
1.01	126	130	136	145	156	158	152	143	508	347	47	−412	−894	−935	−379
1.02	129	133	139	147	159	162	158	141	220	288	11	−442	−920	−963	−427
1.05	138	142	147	155	167	173	172	159	77	2	−102	−517	−978	−1027	−549
1.10	154	157	160	167	178	185	186	179	149	−10	−260	−598	−1014	−1067	−684
1.15	169	171	174	180	188	194	195	190	170	87	−209	−616	−991	−1042	−747
1.20	184	186	188	192	199	203	204	198	183	128	−91	−558	−924	−971	−753
1.30	214	215	216	218	222	224	223	219	208	176	61	−320	−703	−746	−652
1.40	242	243	244	245	247	248	248	245	238	219	155	−87	−434	−485	−480
1.50	270	270	270	271	273	274	275	274	272	262	229	90	−177	−241	−301
1.60	295	295	296	296	298	300	303	304	305	304	291	221	37	−38	−152
1.70	320	320	320	321	323	326	330	334	337	342	344	318	202	117	−48
1.80	343	343	343	344	346	350	356	361	367	376	387	389	320	226	8
1.90	365	365	365	366	369	374	380	386	394	405	422	441	400	293	17
2.00	386	386	386	387	390	395	402	409	417	430	451	478	449	324	−16

Table V. Auxiliary Simple Fluid Values for $(\eta\xi)^{(0)} \times 10^{-3}$

	P_r						
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.55	11379	384	740				
0.60	9151	385	486				
0.65	7325	7402	440	849			
0.70	5748	6016	6055	572	5118		
0.75	4186	4846	4965	512	1225		
0.80	2883	3681	3972	4141	730	2179	
0.85	2448	2446	2902	3262	613	989	
0.90	1051	1592	1817	2249	2685	730	1177
0.93	653	1190	1377	1634	2095	2399	945
0.95		842	1089	1309	1655	1995	850
0.97			748	965	1239	1501	1850
0.98				759	1014	1236	1548
0.99					725	904	1164

Table VI. Auxiliary Size/Shape Deviation Values for $(\eta\xi)^{(1)} \times 10^{-3}$

	P_r						
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.55	33814	−38	−369				
0.60	23989	−46	−143				
0.65	18174	18012	−77	−577			
0.70	14442	13851	13794	−185	−6339		
0.75	12069	10824	10579	−71	−837		
0.80	9288	8747	8226	7918	−176	−1334	
0.85	4232	7097	6616	6076	−11	−147	
0.90	2440	4164	4888	4776	4288	77	326
0.93	856	2301	3105	3751	3659	3355	318
0.95		1381	1951	2671	3139	3000	303
0.97			960	1519	2202	2524	2421
0.98				944	1565	2038	2243
0.99					807	1281	1765

Table VII. Auxiliary Polar Deviation Values for $(\eta\xi)^{(2)} \times 10^{-3}$

	P_r						
T_r	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.55	12963	−43	−574				
0.60	8099	4	−163				
0.65	5786	5657	−32	−673			
0.70	4719	4256	4205	−179	−7048		
0.75	4474	3459	3262	−16	−1033		
0.80	3833	3195	2760	2502	−231	−1952	
0.85	1247	3144	2666	2189	5	−360	
0.90	878	1968	2380	2156	1688	5	−1
0.93	426	968	1510	1893	1694	1400	95
0.95		604	868	1341	1599	1421	134
0.97			471	696	1126	1327	1201
0.98				473	753	1067	1196
0.99					443	643	950

cise care near the saturation line to ensure that the viscosity is indeed calculated for the desired fluid phase regardless of the actual phases of the individual reference fluids. Because the three reference fluids do not obey two-parameter corresponding states, the actual saturation curve for the references may not exactly correspond to the lines drawn. Likewise, the possibility exists that the phase of the test fluid may not correspond to the phase shown in Tables II–IV. To accommondate this possibility, Tables V–VII provide auxiliary values for the region where this may occur. These values are for the opposite phase of those given Tables II–IV. With the full computer program, ELK determines the appropriate phase at the input conditions and finds the correct roots. In the hand implementation of the method, one must know the phase at the desired conditions and choose the auxiliary tables if the phase is opposite that shown in the primary tables.

3. RESULTS OF TESTS

3.1. Nonpolar Fluids

The prediction method has been tested for 36 different nonpolar fluids, a total of 5748 different points, as shown in Table VIII. In this and subsequent tables, N represents the number of experimental points compared, AAD is an absolute average percentage deviation of calculated and

Table VIII. Comparison of Results for Nonpolar Fluids

					ELK		TRAPP	
Fluid	Ref. No(s).	N	T_r	P_r	AAD	Bias	AAD	Bias
Methane	9–14	742	0.55–2.00	0.01–8.81	4.10	1.59	3.61	2.19
Ethane	23–25	370	0.65–1.67	0.02–9.89	2.91	−1.86	2.66	0.71
Propane	13, 26	118	0.58–1.29	0.02–8.11	4.36	−2.87	4.26	−1.70
n-Butane	27, 28	190	0.65–1.20	0.03–9.31	4.50	−1.81	3.53	0.47
Isobutane	29	46	0.76–1.09	0.19–9.44	12.15	−11.37	9.90	−8.30
n-Pentane	30, 31	318	0.63–1.17	0.03–9.02	3.94	−2.81	2.04	0.44
Isopentane	32	289	0.61–1.15	0.03–8.85	6.69	−6.69	6.10	−4.84
Neopentane	33	33	0.72–1.02	0.22–8.62	28.77	−28.77	28.98	−28.98
n-Hexane	34	204	0.59–1.08	0.03–8.42	4.61	−3.11	3.20	−0.33
n-Heptane	16	234	0.55–1.01	0.04–9.24	2.51	−0.27	5.40	4.02
n-Octane	10, 16–19	192	0.57–1.00	0.04–8.14	0.99	0.08	6.62	5.55
Isooctane	32	172	0.55–0.99	0.04–9.73	13.56	−13.56	14.21	−14.14
n-Nonane	35	14	0.56–0.78	0.04–8.56	2.76	−2.76	2.13	1.56
n-Decane	35–37	68	0.56–0.78	0.05–9.75	4.49	−4.41	1.53	0.83
n-Undecane	32	62	0.56–0.81	0.05–7.61	3.56	−2.59	3.16	3.16
n-Dodecane	32	55	0.56–0.79	0.05–8.24	4.47	−4.20	3.04	3.04
n-Tetradecane	35	8	0.57–0.76	0.07–6.81	12.61	−12.61	1.44	−0.91
Ethylene	10	50	1.05–1.50	0.02–8.04	3.60	−2.54	2.70	−0.86
Propylene	10	68	0.80–1.43	0.02–8.81	7.99	−7.84	7.36	−6.13
1-Hexene	32	127	0.56–0.74	0.03–9.46	20.30	20.30	20.23	20.23
1-Heptene	32	120	0.56–0.91	0.04–8.83	10.60	10.47	21.03	21.03
1-Octene	32	98	0.56–0.86	0.04–9.54	7.10	3.01	9.10	7.22
Benzene	14	299	0.58–1.25	0.02–8.18	5.89	−5.69	5.35	−4.69
Toluene	32	212	0.56–0.93	0.02–9.76	5.08	4.96	5.11	5.11
Ethylbenzene	32	148	0.55–0.91	0.03–8.33	2.81	−1.17	1.62	0.25
Cyclohexane	32	233	0.56–0.94	0.02–9.83	41.54	−41.54	43.69	−43.69
Methylcyclohexane	32	198	0.56–0.93	0.29–8.65	26.38	−26.38	28.99	−28.99
Ethylcyclohexane	32	88	0.56–0.85	0.33–8.33	13.81	−13.81	23.04	−23.04
Neon	38, 39	54	0.61–1.80	0.04–3.99	16.17	−15.79	19.62	−18.52
Argon	11, 40, 41	132	0.71–1.98	0.06–9.69	5.49	−5.36	6.69	−4.45
Krypton	42	71	1.42–1.66	0.13–8.96	2.97	−2.88	3.23	−0.30
Xenon	32	84	1.04–1.21	0.02–1.71	5.54	−5.29	3.88	−1.17
Nitrogen	32	228	0.55–1.98	0.03–8.85	5.90	−4.25	6.00	−2.73
Oxygen	32	225	0.58–1.94	0.02–8.93	3.54	−2.86	3.54	−2.60
Fluorine	43	149	0.62–1.87	0.07–4.23	5.98	−0.29	6.07	2.80
Carbon dioxide	44	49	1.03–1.14	0.15–9.35	4.24	1.80	6.66	6.66
Overall		5748	0.55–2.00	0.01–9.89	7.88	−4.45	8.32	−2.77

experimental viscosities, bias is a percentage bias from the mean, and REF indicates the references from which the experimental data were obtained. Also shown in Table VIII are the results from TRAPP. The intent of the comparison is not to establish the superiority of one method over the other. Rather, the intent is to show that for nonpolar fluids ELK predictions are comparable to TRAPP's in accuracy. The predicted values are quite good for most systems, although, as is well known, cycloalkanes and some highly branched aliphatic alkanes do not obey corresponding states very well as indicated by the large biases. It should be emphasized that these results cover a large T_r–P_r range including both liquid and vapor phases.

Illustration of the agreement with experiment over a wide range of temperatures and densities is shown in Figs. 1 and 2. Figure 1 shows very good agreement between predicted and experimental viscosities for liquid *n*-dodecane and illustrates the importance of the size/shape addition to two-parameter corresponding states. A substantial portion of the total viscosity is contributed by the $\alpha(\eta\xi)^{(1)}$ term as seen by the difference between the simple fluid results (dashed line) and the ELK predictions (solid line). In Fig. 2 for gas-phase *n*-pentane, the agreement is quite good at lower densities but deteriorates at higher gas densities. Although not shown on

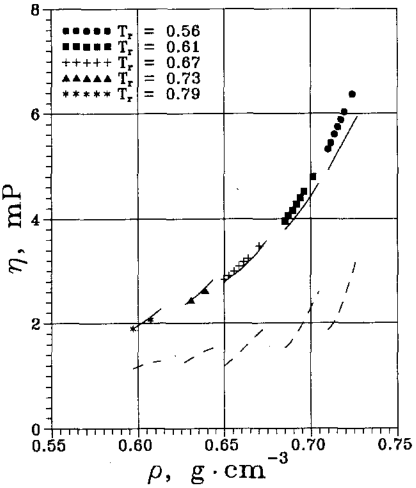

Fig. 1. Comparison of *n*-dodecane liquid viscosities predicted by ELK (solid line) with experimental data at various reduced temperatures. The dashed line represents the contribution from two-parameter corresponding states.

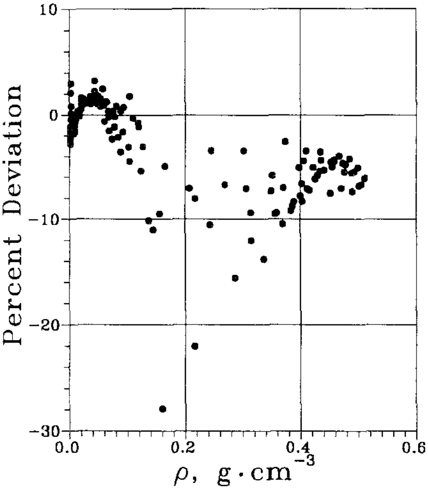

Fig. 2. Percentage deviation between calculated and experimental viscosities of gas-phase *n*-pentane.

this figure, at higher (liquid) densities agreement is again good. The size/shape term affects liquid values much more than vapor, but it is nevertheless essential for calculations of either phase if accuracy is desired. The overall predictions are reasonably good for a general corresponding-states predictive method that is valid for any fluid phase over most of the experimentally accessible P_r–T_r domain. As mentioned, the advantage of ELK is that the same α and β used for thermodynamic property prediction are used for the viscosity calculations, making the method self-consistent.

3.2. Polar Fluids

ELK was also tested on 15 different polar fluids, a total of 1500 different points over a wide range of T_r–P_r as shown in Table IX. The results are quite good for many systems, but some show a significant bias. The same values of β used for thermodynamic calculations are also used for these predictions. The agreement with experimental data for *n*-butyl acetate and dimethyl ether are shown in Figs. 3 and 4, respectively. As can be deduced from Tables II–VII, the polar contribution, $\beta(\eta\xi)^{(2)}$, is quite small in the gas phase except at higher densities. The polar contribution for liquids is more substantial but still not as large as the size/shape contribution except at low temperatures, as illustrated for chlorodifluoromethane in Fig. 5. The relative importance of these effects has been noted before [21].

Table IX. Comparison of Results for Polar Fluids

Fluid	Ref. No.	N	T_r	P_r	ELK		TRAPP	
					AAD	Bias	AAD	Bias
Dimethyl ether	10	87	0.93–1.34	0.02–9.42	3.58	3.01	9.03	8.22
Diethyl ether	10	61	0.87–1.12	0.03–8.13	7.85	7.85	14.54	14.31
Acetone	10	36	0.94–1.06	0.02–8.40	11.42	−7.60	5.74	−5.74
Ammonia	45	82	0.77–1.18	0.01–2.96	8.73	5.77	11.30	1.72
n-Propyl acetate	32	118	0.58–0.91	0.03–8.77	8.67	7.32	13.50	12.99
n-Butyl acetate	32	108	0.55–0.83	0.03–9.31	3.51	−3.42	7.22	7.22
Carbon monoxide	46	12	1.68–1.87	0.36–2.82	1.56	−1.55	2.77	2.77
Dichlorodifluoromethane	32	160	0.65–1.12	0.97–9.41	7.11	−7.10	4.65	−3.33
Chlorodifluoromethane	14, 32	271	0.68–1.28	0.04–7.84	5.75	−1.36	4.71	2.10
1,1,2-Trichloro-1,2,2-trifluoroethane	32	184	0.55–0.99	0.03–8.57	33.41	−33.41	33.40	−33.40
Methanol	10	61	0.83–1.06	0.01–8.77	7.20	−6.27	10.57	1.16
Ethanol	10	94	0.55–1.05	0.02–9.64	11.68	−4.36	18.41	−5.61
n-Propanol	32	150	0.60–1.02	0.02–9.42	10.99	−5.14	21.40	−3.71
Isopropanol	10	48	0.84–1.05	0.02–8.29	8.84	−5.17	8.62	−0.84
Isobutanol	10	28	0.90–1.00	0.02–9.18	4.20	1.14	13.34	8.75
Overall		1500	0.55–1.87	0.01–9.64	10.62	−5.34	13.01	−2.80

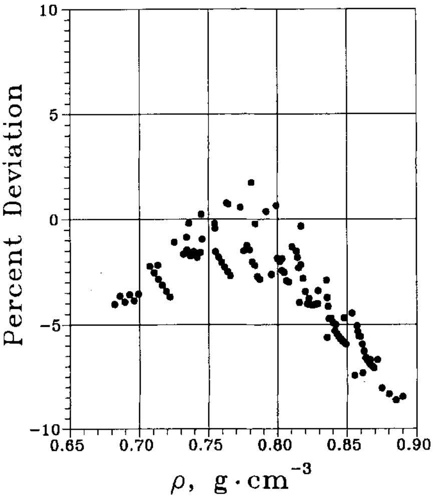

Fig. 3. Percentage deviation between calculated and experimental viscosities of liquid-phase *n*-butyl acetate.

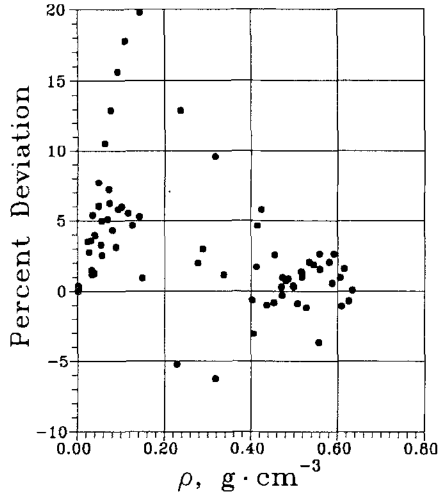

Fig. 4. Percentage deviation between calculated and experimental viscosities of dimethyl ether.

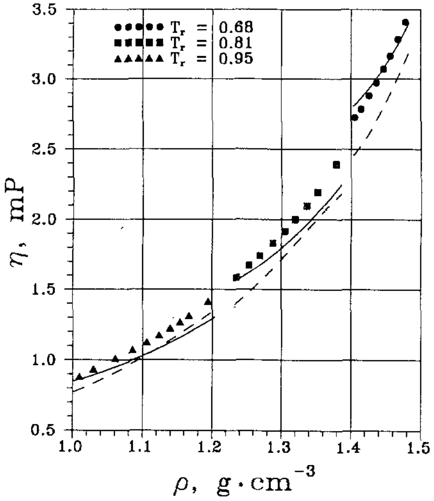

Fig. 5. Comparison of chlorodifluoromethane liquid viscosities predicted by ELK (solid line) with experimental data at various reduced temperatures. The dashed line represents the calculated viscosity without the polar correction term.

3.3. Associating Fluids

ELK predictions for small-chain alcohols are inadequate if α and β values for the monomers are input. A chemical theory was therefore used for alcohols of four carbons or fewer. It is assumed that in the liquid phase, equilibrium is established between the monomeric and the dimeric forms with the equilibrium constant, K, given by

$$K = x_D/x_M^2 \tag{6}$$

where x_D is the mole fraction of dimer and x_M is the mole fraction of monomer. The equilibrium constant is calculated from

$$\ln\left(\frac{K}{K_0}\right) = -\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7}$$

where both the heat of dimerization, ΔH, and the equilibrium constant at the reference temperature T_0 were obtained from Stathis and Tassios [22]. For completeness, these values are tabulated in Table X. Values for α and β for the assumed mixture of monomer and dimer were then calculated from a mole fraction average of the pure values; i.e.,

$$\alpha = x_M\alpha_M + x_D\alpha_D \qquad \text{and} \qquad \beta = x_M\beta_M + x_D\beta_D \tag{8}$$

where the mole fractions are obtained from the solution of Eq. (7) subject to the constraint on the sum of mole fractions. Because no values of α_D and β_D were available for dimerized species, these values were obtained by regression from experimental data and are also included in Table X. Results for fluids assumed to associate are included in Table IX.

Table X. Parameter Values Used for Dimerizing Liquids

Component	α_D	β_D	K_0	ΔH (kJ · mol^{-1})
Methanol	0.46	−0.46	450	−29.29
Ethanol	1.22	0.00	190	−29.29
n-Propanol	1.24	−0.26	90	−29.29
Isopropanol	1.10	−1.28	60	−29.29
Isobutanol	1.38	−0.78	45	−29.29

4. CONCLUSIONS

The extended Lee–Kesler method has been adapted to the calculation of pure-component viscosity of polar and nonpolar fluids. The result is a four-parameter corresponding-states method requiring the critical temperature, the critical pressure, a size/shape parameter α, and a polar interaction parameter β. However, the values of α and β are those previously correlated and tabulated for calculation of equilibrium thermodynamic properties. Thus, the method contains no adjustable parameters and is predictive in nature. With the method, viscosities can be calculated within the range $0.55 \leqslant T_r \leqslant 2.00$ and $0 < P_r \leqslant 10$. Agreement between predicted and experimental viscosities is generally quite good, but there are notable exceptions. Olefins and highly branched and cyclic alkanes do not obey the corresponding-states methodology used either here or in TRAPP very well. For short-chain alcohols, an association model is required which uses empirical values for α_D and β_D. These values are also tabulated in this paper. The method is intended to extend the generalized LK technique to viscosity predictions using only the same fundamental constants currently used for equilibrium properties.

REFERENCES

1. B. I. Lee and M. G. Kesler, *AIChE J.* **21**:510 (1975).
2. W. V. Wilding and R. L. Rowley, *Int. J. Thermophys.* **7**:525 (1986).
3. W. V. Wilding, J. K. Johnson, and R. L. Rowley, *Int. J. Thermophys.* **8**:717 (1987).
4. J. K. Johnson and R. L. Rowley, *Fluid Phase Equil.* **44**:255 (1989).
5. J. K. Johnson and R. L. Rowley, *Int. J. Thermophys.* **10**:479 (1989).
6. J. F. Ely and H. J. M. Hanley, *Ind. Eng. Chem. Fund.* **20**:323 (1981).
7. M. J. Hwang and W. B. Whiting, *Ind. Eng. Chem. Res.* **26**:1758 (1987).
8. L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables* (Hemisphere, New York, 1984).
9. J. P. Boon, J. C. Legros, and G. Thomaes, *Physica* **33**:547 (1967).
10. I. F. Golubev, *Viscosity of Gases and Gas Mixtures, a Handbook* (Israel Program for Scientific Translations, Jerusalem, 1970).
11. W. M. Haynes, *Physica* **67**:440 (1973); *Physica* **70**:410 (1973).
12. J. Hellemans, H. Zink, and O. Van Paemel, *Physica* **46**:395 (1970).
13. E. T. S. Huang, G. W. Swift, and F. Kurata, *AIChE J.* **12**:932 (1966).
14. N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed. (John Wiley and Sons, New York, 1975).
15. J. A. Jossi, L. I. Stiel, and G. Thodos, *AIChE J.* **8**:59 (1962).
16. N. A. Agaev and I. F. Golubev, *Gazov. Promst.* **8**:50 (1963).
17. L. T. Carmichael and B. H. Sage, *AIChE J.* **12**:559 (1966).
18. J. C. McCoubrey, J. N. McCrea, and A. R. Ubbelohde, *J. Chem. Soc.* 1961 (1951).
19. R. M. Melaven and E. Mack, Jr., *J. Am. Chem. Soc.* **54**:888 (1932).

20. K. J. Okeson, *A Four-Parameter Corresponding-States Method for the Prediction of Newtonian, Pure-Component Viscosity*, M.S. thesis (Brigham Young University, Provo, Utah, 1989).
21. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases & Liquids*, 4th ed. (McGraw–Hill, New York, 1987).
22. P. J. Stathis and D. P. Tassios, *Ind. Eng. Chem. Process Dev.* **24**:701 (1985).
23. L. T. Carmichael and B. H. Sage, *J. Chem. Eng. Data* **8**:94 (1963).
24. D. D. Diller and J. M. Saber, *Physica* **108A**:143 (1981).
25. B. E. Eakin, K. E. Starling, J. P. Dolan, and R. T. Ellington, *J. Chem. Eng. Data* **7**:33 (1962).
26. L. T. Carmichael, V. M. Berry, and B. H. Sage, *J. Chem. Eng. Data* **6**:411 (1964).
27. L. T. Carmichael and B. H. Sage, *J. Chem. Eng. Data* **8**:612 (1963).
28. J. P. Dolan, K. E. Starling, A. L. Lee, B. E. Eakin, and R. T. Ellington, *J. Chem. Eng. Data* **8**:396 (1962).
29. M. H. Gonzalez and A. L. Lee, *J. Chem. Eng. Data* **11**:357 (1966).
30. N. A. Agaev and I. F. Golubev, *Gazov. Promst.* **8**:45 (1963).
31. A. L. Lee and R. T. Ellington, *J. Chem. Eng. Data* **10**:101 (1965).
32. K. Stephan and K. Lucas, *Viscosity of Dense Fluids* (Plenum Press, New York, 1979).
33. M. H. Gonzalez and A. L. Lee, *J. Chem. Eng. Data* **13**:66 (1968).
34. N. A. Agaev and I. F. Golubev, *Dokl. Phys. Chem.* **151**:597 (1963).
35. Y. L. Rastorguyev and A. S. Keramidi, *Fluid Mech. Sov. Res.* **3**:156 (1974).
36. L. T. Carmichael, V. M. Berry, and B. H. Sage, *J. Chem. Eng. Data* **14**:27 (1969).
37. A. L. Lee and R. T. Ellington, *J. Chem. Eng. Data* **10**:346 (1965).
38. J. M. J. Coremans, A. Van Itterbeek, J. J. M. Beenakker, H. F. P. Knaap, and P. Zandbergen, *Physica* **24**:557 (1958).
39. W. Herreman and W. Grevendonk, *Cryogenics* **14**:395 (1974).
40. G. P. Flynn, R. V. Hanks, N. A. Lemaire, and J. Ross, *J. Chem. Phys.* **38**:154 (1963).
41. A. Michels, A. Boltzen, and W. Schuurman, *Physica* **20**:1141 (1954).
42. N. J. Trappeniers, A. Boltzen, J. Van Oosten, and H. R. Van Den Berg, *Physica* **31**:945 (1965).
43. W. M. Haynes, *Physica* **76**:1 (1974).
44. A. Michels, A. Boltzen, and W. Schuurman, *Physica* **23**:95 (1957).
45. L. T. Carmichael, H. H. Reamer, and B. H. Sage, *J. Chem. Eng. Data* **8**:400 (1963).
46. A. K. Barua, M. Afzal, G. P. Flynn, and J. Ross, *J. Chem. Phys.* **41**:374 (1964).